



Preparation of visible-light-responsive photocatalyst by dehydronitritization of gallium oxide hydroxide for hydrogen evolution from water

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ABSTRACT

We have performed dehydronitritization of GaOOH under NH₃ flow to produce nitrogen doped Ga₂O₃ and examined their photocatalytic activities for H₂ evolution from an aqueous methanol solution under visible light irradiation. GaOOH was synthesized by hydrothermal treatment and dehydronitritized at a temperature ranging from 773 K to 1273 K under NH₃ flow. At first, GaOOH was dehydrided to Ga₂O₃ under 873 K and followed nitritization. With increasing dehydronitritization temperature, the products were getting closer to full nitride (GaN). Among all dehydronitritized samples, only one sample sintered at 1173 K showed photocatalytic activity under visible light irradiation and its crystalline structure had not changed before and after the reactions, while other samples did not show the activity and were oxidized to GaOOH. From thermodynamical aspect, if nitrogen dissolved into oxide or making oxynitride, its chemical potential must be lower than that of N in GaN. Therefore, there should be some gallium oxynitride phase like GaN_yO_{3-x} stable in water showing photocatalytic activity.

1. Introduction

Photocatalytic reduction of water or CO₂ with solar radiation has attracted a lot of interests and various photocatalysts have been developed [1–8]. Recently, gallium oxide (Ga₂O₃), a wide gap semiconductor, has been often used as the photocatalyst [2,8–13]. However, since the band gap of Ga₂O₃ is too large to use solar radiation effectively, various modifications have been made for narrowing its band gap. R. Asahi et al. [13,14] have reported that nitriding of metal oxides can reduce their band gap providing a visible-light response, because N 2p orbitals are newly formed above O 2p orbitals in their valence band and succeeded to enhance the photocatalytic activity. Che-Chia Hu et al. [15,16] have reported that nitrogen doped Ga₂O₃ prepared from Ga₂O₃ or GaON prepared from Ga(OH)₃ showed the activities for H₂ evolution from an aqueous methanol solution.

In previous works [17,18], we have found that without an Ag cocatalyst, Ga₂O₃ consisting of two phases (β and γ) shows higher photocatalytic activity for CO₂ reduction with water under ultra violet (UV) irradiation compared with commercially available Ga₂O₃. In order to generate visible light response in Ga₂O₃ photocatalysts, we have performed nitriding of Ga₂O₃ consisting of β and γ phase by calcination under ammonia (NH₃) atmosphere. However, under visible light irradiation, thus nitrided Ga₂O₃ did not show the activity even for water

splitting [19].

Using gallium oxide hydroxide (GaOOH) as a precursor, synthesis of Ga₂O₃ has been demonstrated [20–23]. Until now, however, GaOOH has been seldom used as a precursor for synthesis of nitrogen doped Ga₂O₃ or GaN for photocatalytic water splitting under visible light irradiation. All above mentioned motivate us to synthesize a new catalyst with dehydronitritization of GaOOH made by ourselves under NH₃ atmosphere at temperature ranging from 773 K to 1273 K, which works as a photocatalyst for water splitting under visible light, as a preliminary step to make the photocatalyst for CO₂ reduction under visible light. For examination of the photocatalytic activity of the synthesized samples for water splitting under visible light irradiation, H₂ evolution from an aqueous methanol solution was tested with a Pt cocatalyst. The samples were characterized with X-ray diffraction (XRD), N K-edge XANES, O K-edge XANES, Ga K-edge EXAFS and UV–vis diffuse reflectance spectra measurements. Morphology of the samples were observed by SEM.

2. Experimental

2.1. Sample preparation

In the present study, home synthesized GaOOH was dehydronitritized

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(heated under ammonia flow) at various temperatures. Synthesis of GaOOH was done with the following way. First, 3.0 g of Ga(NO₃)₃ · 8H₂O (Kishida Chemical, 99.0%) was dissolved in 25 mL of distilled water and ultrasonically treated for several minutes followed by addition of 25 mL of aqueous ammonia solution (Kishida Chemical, 28%) to make a precursor. Then, the precursor was hydrothermally treated in a Teflon-lined autoclave at 393 K for 6 h. After the hydrothermal treatment, resultant products were filtered and washed with 200 mL of distilled water and dried for overnight to get GaOOH powder. The GaOOH was subjected to dehydronitridization under continuous flow of NH₃ gas (60 mL/min) at temperature ranging from 773 K to 1273 K for 15 h. As a cocatalyst, Pt was loaded on the dehydronitrized GaOOH powder by photodeposition under UV light irradiation (1.0 mW/cm²) for 30 min using an aqueous H₂PtCl₆ (Wako Pure Chemical, 99.9%) solution. Then, the powder was filtered with distilled water and dried at room temperature. The dehydronitrized GaOOH powder with the Pt cocatalyst thus obtained were referred as samples with S(XK) (X: dehydronitridization temperature in Kelvin) hereafter.

2.2. Characterization

Diffuse reflectance (DR) UV–vis spectra were measured using UV–vis spectrophotometer (JASCO, V-670). As the reference, the spectra of BaSO₄ (Kishida Chemical) powder was used. The crystalline structures of the samples were investigated by X-ray diffraction (XRD) analysis. XRD patterns of the samples were recorded on a MiniFlex600 (Rigaku) using Cu Kα as the radiation source with an operating voltage of 40 kV and current of 15 mA at room temperature. The XRD patterns were collected at 2θ angles in the range of 20–60°. The 2θ step size was 0.02° with an angle scanning rate of 10°/min. The morphology of the samples was examined by FE-SEM (JSM-6500 F FE-SEM) at Osaka City University. N K-edge and O K-edge XAFS spectra of the samples were obtained at BL4B of the UVSOR facility in sample current mode and Ga K-edge XAFS at BL551 of Aichi Synchrotron Radiation Center in transmission mode at room temperature.

2.3. Photocatalytic reaction

Photocatalytic H₂ evolution test was conducted in a specially designed gas-liquid-solid three phase reactor cell [8–12,17,18] under visible light irradiation. In the reactor cell, the sample (0.1 g) was dispersed in 10 mL aqueous methanol solution containing 20 vol% methanol for H₂ evolution. The product of H₂ was detected with an online gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Shimadzu GC-8APT). Before the test, the reactor cell was filled with the aqueous methanol solution and exposed to He gas with its flow rate of 100 mL/min. After 1 h test, He flow rate was changed to 3 mL/min. Then H₂ was measured as the background without visible light irradiation. Subsequently, photocatalytic H₂ evolution tests under irradiation of visible-light, given by a 300 W Xe lamp with a cut filter for λ > 420 nm, were started and H₂ production rates were recorded each 1 h for the total of 5 h. The visible light intensity measured in the range of 415 ± 55 nm was 127 mW/cm².

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of dehydronitrized samples. The crystalline structures of S(773 K) and S(873 K) were assigned to be a single phase of α-Ga₂O₃. This indicates that even under NH₃ atmosphere dehydration of GaOOH occurred first and is consistent with the observation by L. Shi et al. [20] that Ga₂O₃ was obtained by pyrolysis of GaOOH at above 683 K. In addition, we have succeeded nitriding of Ga₂O₃ without changing their crystalline structures, i.e. although the samples contained nitrogen, their XRD patterns did not change before and after dehydronitridization under 823 K. Thus, Ga₂O₃ produced by dehydration of GaOOH was crystalized to be α-Ga₂O₃

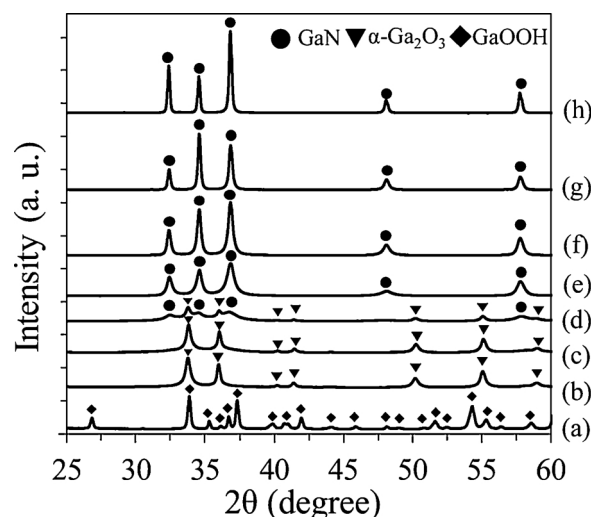


Fig. 1. XRD patterns of (a)GaOOH (b)S(773 K) (c)S(873 K) (d)S(973 K) (e)S(1073 K) (f)S(1173 K) (g)S(1273 K) (h)GaN(ref).

single phase as indicated in the X-ray diffraction patterns. Since the full width half maximum of S(873 K) was smaller than that of S(773 K), nitriding of S(873 K) was more proceeded compared to that of S(773 K). GaN phase appeared in the X-ray diffraction patterns of S(973 K). With increasing dehydronitridization temperature, GaN phase grew, and above 1073 K the oxide disappeared resulting single phase of GaN. Crystallinity of the GaN phase became better with increasing dehydronitridization temperature as appeared in sharper X-ray diffraction peaks. The relative intensity changes of three dominant peaks of GaN should reflect changes of particle shapes and sizes together with crystallinity as observed in Fig. 2. However, no clear correlation was found among them.

Surface morphology of synthesized GaOOH and dehydronitrized samples was observed by SEM as shown in Fig. 2. The synthesized GaOOH (Fig. 2(a)) showed a rod-like shape with rather smooth surfaces. Although S(1173 K) remained the rod-like structure of GaOOH, their surfaces became rough and seemed to be divided into small particles, probably corresponding to nucleation and growth of Ga₂O₃ grains on the rod of GaOOH (Fig. 2(b)).

The local structures of all dehydronitrized samples were investigated by Ga K-edge EXAFS analysis. The Fourier transform was performed on each EXAFS spectrum in the range from 3 Å⁻¹ to 12 Å⁻¹ and the radial structure function (RSF) was obtained as shown in Fig. 3. A peak appeared at 1–2 Å was assigned to the backscattering from adjacent oxygen or nitrogen atoms (Ga–O or Ga–N bond), and a peak around 3 Å shows the presence of the second-neighboring gallium atoms (Ga–(O or N)–Ga bond). The backscattering amplitude and phase shift of oxygen and nitrogen atoms are almost the same. This inhibits the distinction of Ga–O and Ga–N bonds and makes discussion about the formation of Ga–N bonds difficult. However, changes in local structure surrounding Ga atoms could be derived as follows from RSF together with the XRD analysis (see Fig. 1.) Although S(773 K) and S(873 K) show similar RSF, the peak around 3 Å of S(873 K) was smaller than that of S(773 K). This suggests that more Ga–N bonds were formed in Ga₂O₃ phase in S(873 K) compared with that in S(773 K) and is consistent with XRD patterns analysis i.e. the increase of the number of Ga–N bond in S(873 K) made the full width half maximum of S(873 K) smaller than that of S(773 K). On the other hand, a large peak around 3 Å newly appeared for samples dehydronitrized above 973 K, which was attributed to Ga–N–Ga bond formation, referring RSF of commercially available GaN. Above 1073 K, the number of Ga–N–Ga bonds increased corresponding to the completion of nitriding (full GaN formation) as indicated in the XRD pattern.

Fig. 4 shows DR UV–vis spectra of all dehydronitrized samples. The spectra intensities were converted to the Kubelka-Munk function. DR

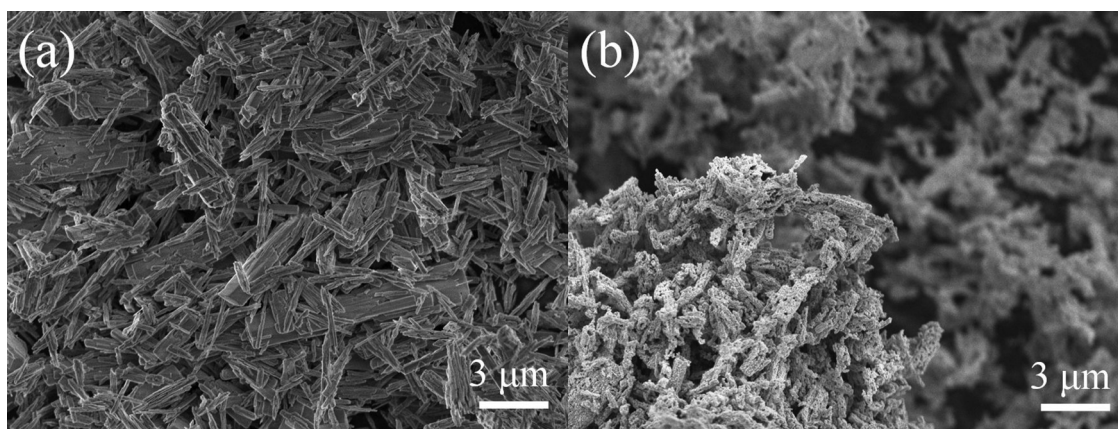


Fig. 2. SEM images of (a)GaOOH (b)S(1173 K).

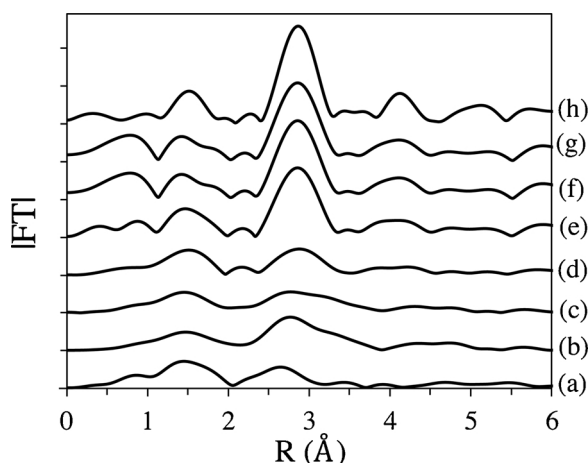


Fig. 3. Radial structure functions for Ga K-edge EXAFS spectra of (a)GaOOH (b) S(773 K) (c)S(873 K) (d)S(973 K) (e)S(1073 K) (f)S(1173 K) (g)S(1273 K) (h)GaN(ref).

spectra of the samples exhibited absorption bands in visible light region after the dehydronitriding. When dehydronitriding temperature was under 973 K, the absorption edge of the samples shifted to longer wavelength region with increasing dehydronitriding temperature. However, when dehydronitriding temperature was above 973 K, the absorption edge shifted to shorter wavelength region. It is noticeable that S(973 K) showed the largest red-shift. Similar red-shift was observed and

attributed to the formation gallium oxy-nitride (GaON) by Che-Chia Hu et al. [15] for samples prepared by nitriding of $\text{Ga}(\text{OH})_3$ under NH_3 flow [15]. They have reported that the bandgap of GaON is much smaller than that of GaN because p-d repulsion between $\text{N}2\text{p}/\text{O}2\text{p}$ and $\text{Ga}3\text{d}$ occurs in GaON valence band, thus shifting upward the top of the valence band level and reducing the GaON band gap. Although the formation of the GaON phase was not confirmed in the X-ray diffraction patterns, a new phase like gallium oxy-nitride (referred as $\text{GaN}_y\text{O}_{3-x}$ hereafter) is likely formed or nitrogen/oxygen atoms are dissolved in oxide/nitride phase as a new thermodynamically stable phase.

Local structure of doped nitrogen was also examined by N K-edge XANES measurement as shown in Fig. 5. Peaks at around 404.8 and 407.0 eV are related to the transitions between $1\text{s}-2\text{p}_{x,y}$ and $1\text{s}-2\text{p}_z$ orbital, respectively [24–26] and they became sharper as dehydronitriding temperature increased. This confirms that the nitriding proceeded with increasing the temperature. In addition to N K-edge XANES measurements, O K-edge XANES measurements were carried out to investigate the chemical states of oxygen near the surface. (See Fig. 6) All dehydronitrided samples are clearly distinguished from GaOOH. The XANES feature of S(773 K) was similar to that of Ga_2O_3 [10] and the other dehydronitrided samples except S(1273 K) exhibited O K-edge XANES peak around 534 eV while that of the S(1273 K) shifted to 535 eV. As the peak around 534 eV grows with increasing dehydronitriding temperature, this peak would correspond to O atoms neighbored to N atoms, i.e. oxide phase doped with N atoms. On the other hand, 535 eV peak, which also appeared in GaN(ref), would be originated from O atoms on GaN surface, i.e. surface of GaN is oxidized. Higher energy shifts suggest weaker bonding of Ga–O in GaN compared

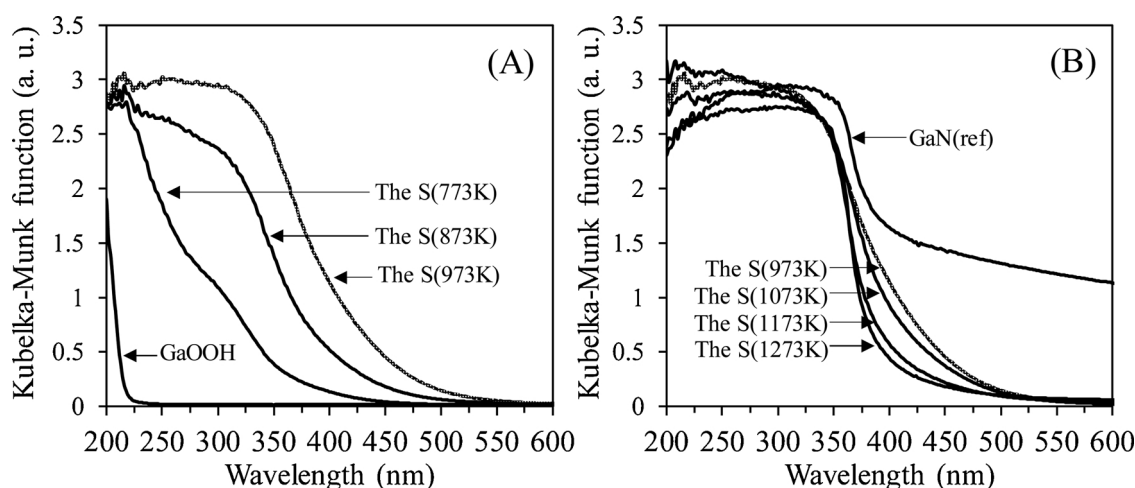


Fig. 4. DR UV-vis spectra of dehydronitrided samples.

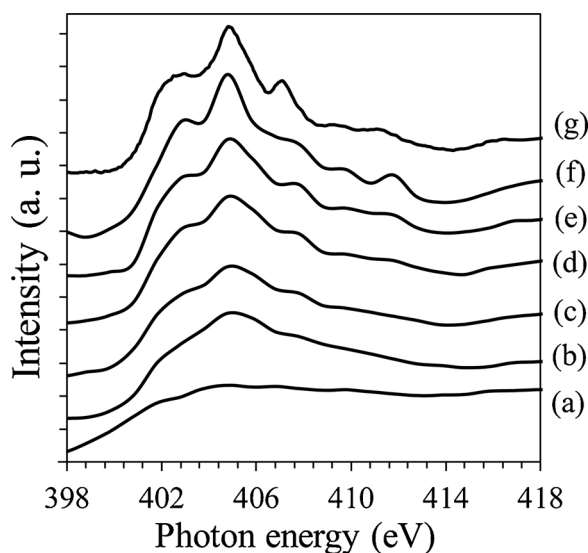


Fig. 5. N K-edge XANES spectra of (a)S(773 K) (b)S(873 K) (c)S(973 K) (d)S(1073 K) (e)S(1173 K) (f)S(1273 K) (g) GaN(ref).

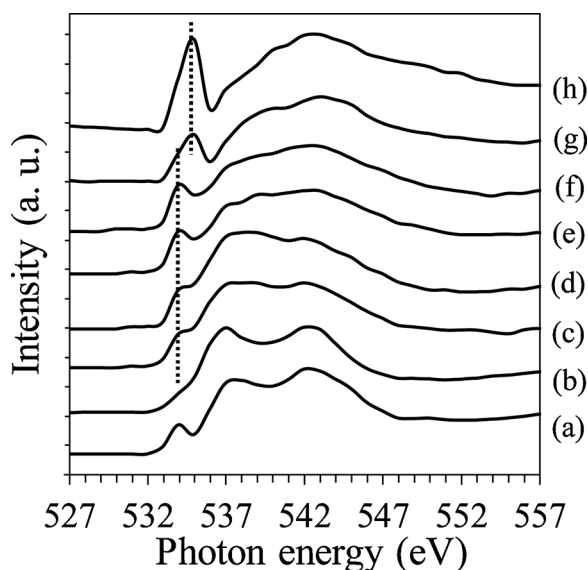


Fig. 6. O K-edge XANES spectra of (a)GaOOH (b)S(773 K) (c)S(873 K) (d)S(973 K) (e)S(1073 K) (f)S(1173 K) (g)S(1273 K) (h) GaN(ref).

to Ga-O in Ga_2O_3 . In O K-edge XANES, GaN and S(1273 K) can be separated from the others. This indicates that nitriding of S(1273 K) was fully proceeded, while the others still retained oxygen in the nitride and/or forming $\text{GaN}_x\text{O}_{3-x}$ like structure. Thus, the K-edge XANES analysis which is surface sensitive, clearly showed the difference of chemical nature of O and N atoms in near surface region between S(1173 K) and S(1273 K).

Photocatalytic H_2 evolution tests under visible light irradiation were conducted using the 0.5 wt% Pt loaded S(973 K), S(1073 K), S(1173 K) and S(1273 K). The visible light was given by a 300 W Xe lamp through a cut-off mirror with cut-off wavelength of 380 nm. As summarized in Table 1, only Pt loaded S(1173 K) showed the activity for H_2 evolution under visible light irradiation while other samples were inactive. We conducted XRD analysis for all samples after the tests. As seen in Fig. 7, only S(1173 K) which showed photocatalytic activity fundamentally maintained its original XRD patterns, while all other samples significantly changed in their XRD patterns. The XRD pattern changes were most likely caused by oxidation of the nitride phase and/or GaOOH formation during the photocatalytic H_2 evolution tests. It is

Table 1
Photocatalytic H_2 evolution over the dehydronitrided samples under visible light irradiation.

Sample	H_2 production rate ($\mu\text{mol/h}$)
GaN(ref)	N.D.
S(1273 K)	N.D.
S(1173 K)	0.80
S(1073 K)	N.D.
S(973 K)	N.D.

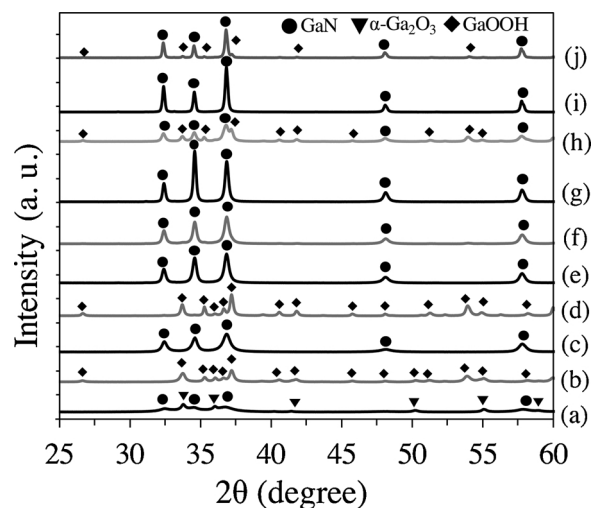


Fig. 7. XRD patterns of S(973 K) (a)before (b)after, S(1073 K) (c)before (d) after, S(1173 K) (e) before (f) after, S(1273 K) (g) before (h) after and GaN(ref) (i) before (j) after.

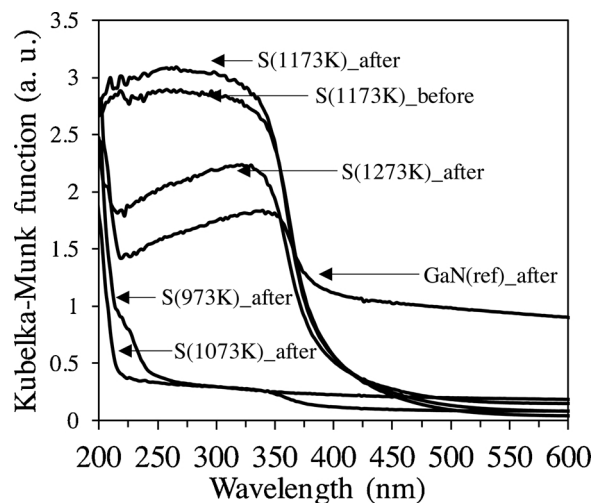


Fig. 8. DR UV-vis spectra of dehydronitrided samples after the reactions.

well known that, in nitride and oxynitride materials, nitrogen atoms in the surface region were oxidized by photogenerated holes during the reaction and released from the samples ($2\text{N}^{3-} + 6\text{h}^+ \rightarrow \text{N}_2$) [27,28]. After the tests, DR UV-vis spectra (Fig. 8) for all samples except S(1173 K) exhibited sharp absorption around 200 nm, which well corresponds to the formation of GaOOH as seen in Fig. 4(A). The XRD patterns after the tests also clearly indicate the formation GaOOH after the photocatalytic H_2 evolution test. Only S(1173 K) which showed H_2 activity did not change its structure indicating its crystalline structure was stable under the atmosphere of the tests.

The reason for the appearance of photocatalytic activity and structure stability only for S(1173 K) is not clear. Nevertheless, the present

results suggest the importance of chemical state of nitrogen. Since GaN does not show catalytic activity, nitrogen bonding in the active sample should be modified from that of GaN but stable. From thermodynamical aspect, if N atoms dissolved in oxide or making $\text{GaN}_y\text{O}_{3-x}$, their chemical potential must be lower than that of N in GaN. This support the formation of $\text{GaN}_y\text{O}_{3-x}$ with N chemically stable together with O. Although the existence of $\text{GaN}_y\text{O}_{3-x}$ or something like GaON has been suggested by Che-Chia Hu *et al.* [15], its chemical form and micro-structure are not clear. Nevertheless it is hardly oxidized in water under visible light irradiation. Most probably S(1173 K) is exhibiting this phase. In other words, with using an appropriate sintering technique, some gallium oxynitride phase like $\text{GaN}_y\text{O}_{3-x}$ can be produced as a stable phase. To produce this phase, there could be more suitable temperature of nitriding or starting materials which remain for future studies.

4. Conclusion

We have succeeded to produce a new photocatalyst having $\text{GaN}_y\text{O}_{3-x}$ like phase for H_2 evolution under visible light irradiation with dehydronitridation of our synthesized GaOOH under NH_3 flow at a given temperature from 773 K to 1273 K. Among all prepared samples, only one sample dehydronitrided at 1173 K shows photocatalytic activity for H_2 evolution from an aqueous solution of methanol solution under visible light irradiation ($\lambda > 420$ nm). Samples dehydronitrided below and above 1173 K hardly showed the photocatalytic activity.

Comparison of X-ray analysis for all samples before and after the H_2 evolution tests has shown that, only the active sample remained its original crystalline structure after the H_2 evolution test and the other samples exhibited significant change in their crystalline structure, showing formation of GaOOH. The samples dehydronitrided at lower temperature might not be well crystallized (sintered) and likely unstable in water. However, the sample dehydronitrided at 1273 K which was well crystallized to be GaN, also showed structure changes to GaOOH. This indicates that GaN crystalline is not stable in water under visible light irradiation. Since N dissolved in Ga_2O_3 or something like $\text{GaN}_y\text{O}_{3-x}$ should be, from thermodynamical aspect, more stable compared to N in GaN, there could be some suitable or appropriate chemical state of N in Ga_2O_3 or $\text{GaN}_y\text{O}_{3-x}$ which would be hardly oxidized in water.

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